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(54) Title: METHOD OF MAKING WINDOW UNIT

(57) Abstract: A method of making a window unit is provided which may result in improved yields. In certain example embodiments, the method involves coating a substrate with both (i) a solar control/management coating, and (ii) a protective layer (e.g., of or including diamond-like carbon (DLC) over the solar control/management coating. The protective layer protects the coated substrate from scratches and/or the like during processing prior to heat treatment. Then, during heat treatment, the protective layer(s) is burned off in part or in whole. Following heat treatment, the coated article (substrate with solar control/management coating thereon) is coupled to another substrate in order to form the window unit.

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## TITLE OF THE INVENTION

## METHOD OF MAKING WINDOW UNIT

[0001] This invention relates to a method of making a window unit (e.g., IG window unit). More particularly, this invention relates to a method of making a window unit in which a temporary protective layer (e.g., of or including diamond-like carbon (DLC)) is provided over a solar control coating so that the coated article can be protected from scratches or the like during processing, with the temporary protective layer subsequently being burned off during heat treatment (e.g., thermal tempering or heat bending) prior to use of the final resulting product.

## BACKGROUND OF THE INVENTION

[0002] Insulating glass (IG) window units typically include first and second glass substrates spaced apart from one another via at least one spacer so as to define a gap therebetween. For example, see U.S. Patent No. 5,557,462. The gap between the glass substrates may or may not be evacuated and/or filled with gas in different instances. As in the '462 patent, one of the glass substrates of the IG window unit is often coated with a solar control/management coating (e.g., a low-E coating). Solar control/management coatings typically include at least one layer (e.g., of or including Ag, Au, NiCr, and/or the like) that reflects infrared (IR) and/or ultraviolet (UV) radiation. Example solar control/management coatings may be found, for example and without limitation, in any of U.S. Patent Nos. 3,682,528; 4,898,790; 5,376,455; 5,377,045; 5,514,476; 5,557,462; 5,688,585; 5,770,321; 5,902,505; 5,942,338; 6,059,909; 6,060,178; 6,132,881; or 6,159,607.

[0003] IG window units are typically made in the following manner. A first glass substrate is coated (e.g., via sputtering or the like) with a solar control/management coating, and processed as follows. The coated glass substrate may be shipped (e.g., via truck, train, ship, plane, or the like) from the coating facility to an IG manufacturing facility, and put in inventory using a forklift or the like. Subsequently, a forklift may move the coated substrate from its inventory location to a cut-down line where the coated substrate is cut to size. The cut coated substrate

may then be seamed, washed, and heat treated (e.g., thermally tempered). Thereafter, the coated substrate is coupled to another glass substrate via at least one spacer so as to form an IG window unit.

[0004] Unfortunately, during the course of such processing between coating and heat treatment, the coated substrate is moved on numerous occasions and is subject to damage (e.g., scratching). Low-E coatings are often soft and tend to be prone to damage in this regard such as scratching. Yields have been found to suffer due to coated substrates which are damaged (e.g., scratched or otherwise rendered non-useable) between coating and heat treatment.

[0005] In view of the above, it will be appreciated by those skilled in the art that there exists a need in the art for an improved method of making window units (e.g., IG units, vehicle windshields, and/or the like) which include at least one coated substrate.

## BRIEF SUMMARY OF THE INVENTION

[0006] An object of this invention is to provide an improved method of making insulating glass (IG) window units.

[0007] Another object of this invention is to provide an improved method of making vehicle windshields. The method is also applicable to other types of windows, monolithic and/or laminated.

[0008] Another object of this invention is to provide a method of making a window unit (e.g., IG unit and/or vehicle windshield) which results in improved yields. In certain example embodiments of this invention, the method involves coating a substrate with both (i) a solar control/management coating, and (ii) at least one protective layer (e.g., of or including diamond-like carbon (DLC)) over the solar control/management coating. The protective layer(s) protects the coated substrate from scratches and/or the like during processing prior to heat treatment (HT). Then, during heat treatment, the protective layer(s) is burned off in part or in whole. Following heat treatment, the coated article (substrate with solar control/management coating thereon) is coupled to another substrate in order to form the window unit.

[0009] Another object of this invention is to fulfill one or more of the above-listed objects and/or needs.

[0010] Certain example embodiments of this invention fulfill one or more of the above-listed objects and/or needs by providing a method of making a window unit, the method comprising: providing a solar control coating on a glass substrate; depositing a temporary protective layer on the glass substrate over the coating, the temporary protective layer having an average hardness of at least 10 GPa; heat treating the substrate with the coating and protective layer thereon at a temperature of at least 570 degrees C so that the protective layer burns off; and following said heat treating, coupling the glass substrate with the coating thereon to another substrate in order to form the window unit.

[0011] Other example embodiments of this invention fulfill one or more of the above-listed objects and/or needs by providing a method of making a window unit, the method comprising: providing a coating on a glass substrate, the coating including at least one layer comprising Ag; depositing a protective layer comprising diamond-like carbon (DLC) on the substrate over the coating; heat treating the substrate with the coating and protective layer thereon so that the protective layer comprising diamond-like carbon (DLC) at least partially burns off during the heat treating; and following said heat treating, coupling the glass substrate with the coating thereon to another substrate in order to form the window unit.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIGURE 1 is a cross sectional view of an IG window unit according to an example embodiment of this invention.

[0013] FIGURE 2 is a cross sectional view of a vehicle windshield according to an example embodiment of this invention.

[0014] FIGURES 3(a), 3(b), 3(c) and 3(d) are cross sectional views progressively illustrating how a window unit is made according to an example embodiment of this invention.

[0015] FIGURE 4 is a flowchart illustrating steps showing how a window unit is made according to an example embodiment of this invention.

[0016] FIGURE 5 is a cross sectional view of a coated substrate at a point in time during the manufacturing process according to an example embodiment of this invention, at which point in time the substrate is coated with both a solar control coating and a temporary protective layer(s) (the precise illustrated coating is provided for purposes of example only).

[0017] FIGURE 6 is a cross sectional view of a coated substrate at a point in time during the manufacturing process according to another example embodiment of this invention, at which point in time the substrate is coated with both a solar control coating and a temporary protective layer(s) (this precise illustrated coating is provided for purposes of example only).

#### DETAILED DESCRIPTION OF EXAMPLE EMBODIMENTS OF THE INVENTION

[0018] Referring now more particularly to the accompanying drawings in which like reference numerals refer to like parts/layers throughout the several views. The instant invention relates to methods of making window units including but not limited to insulating glass (IG) window units and vehicle windshields. Initially, before describing methods according to example embodiments of the instant invention, reference is made to Figs. 1-2 which illustrate example window units which may be made according to different example embodiments of this invention.

[0019] Fig. 1 is a cross sectional view of an insulating glass (IG) window unit which may be made in certain example embodiments of this invention. The IG window unit includes first glass substrate 1 and second glass substrate 2 which are spaced apart from one another by one or more spacers 4. Each of substrates 1 and 2 is from about 1.0 to 10.0 mm thick, more preferably from about 1.8 mm to 4 mm thick. Spacer(s) 4 may be provided around the edge/periphery of the window unit as in conventional IG window units, or alternatively may be provided in an array throughout the viewing area of the window unit as in vacuum IG window units. Spacer(s) 4 function to space the substrates 1 and 2 from one another so as to define

space 6 therebetween. Space 6 may be at atmospheric pressure or lower in different embodiments of this invention, and may or may not be filled with gas. While substrates 1 and 2 are of glass in preferred embodiments of this invention, they may be of other materials such as plastic in alternative embodiments of the invention. The IG window unit of Fig. 1 has a visible transmission of at least about 30% in certain example embodiments of this invention, more preferably at least about 60%, and most preferably at least about 70%.

[0020] Figure 2 is a cross sectional view of a vehicle windshield which may be made in certain example embodiments of this invention. The windshield includes first glass substrate 1 and second glass substrate 2 that are laminated together via a polymer inclusive interlayer 8. Interlayer 8 may be of or include polyvinyl butyral (PVB), polyvinyl chloride, polypropylene, polyethylene, polyurethane, or any other suitable laminating material. The windshield of Fig. 2 preferably has a visible transmission of at least 70%, more preferably of at least 75%.

[0021] Still referring to Figs. 1-2, each of these window units includes at least one solar control/management coating 27 for reflecting certain amounts of infrared (IR) and/or ultraviolet (UV) radiation. While coating 27 is provided on the interior surface of substrate 1 in Figs. 1-2, the coating 27 may instead be provided on the interior surface of the other substrate 2 in alternative embodiments of this invention. Moreover, in other embodiments of this invention it is possible to provide a solar control/management coating 27 on each of substrates 1-2. Coating 27 may include one or more layers in different embodiments of this invention, although a multi-layered coating 27 is preferred.

[0022] The phrases "solar control coating" and "solar management coating" herein mean that the coating includes at least one layer of a material (e.g., Ag, Au, and/or NiCr) that functions to reflect certain amounts of UV and/or IR radiation. Example solar control coatings 27 are shown in Figs. 5-6. Moreover, solar control coating 27 may comprise any of the coatings described and/or illustrated in any of U.S. Patent Nos. 3,682,528; 4,898,790; 5,376,455; 5,377,045; 5,514,476; 5,557,462; 5,688,585; 5,770,321; 5,902,505; 5,942,338; 6,059,909; 6,060,178; 6,132,881; or 6,159,607, or may comprise any other suitable solar control coating.

[0023] Figures 3-4 illustrate a method of making a window unit (e.g., IG unit or windshield) according to an example embodiment of this invention. In this regard, for purposes of example, a process for making an IG window unit according to an example embodiment of this invention will now be described.

[0024] As shown in Fig. 3(a), a first glass substrate 1 (e.g., soda-lime-silica glass, borosilicate glass, or any other suitable type of glass) is coated with a solar control/management coating 27 (see step A in Fig. 4). Coating 27 may be deposited on substrate 1 via sputtering or any other suitable technique. Thereafter, as shown in Fig. 3(b), at least one temporary protective layer 29 is deposited on the substrate 1 over solar control/management coating 27 (see step B in Fig. 4). Protective layer(s) 29 may or may not directly contact coating 27 in different embodiments of this invention (i.e., other layer(s) may be provided between coating 27 and layer 29). Layer 29 may be from about 5 to 3,000 Å thick in certain example embodiments of this invention, more preferably from about 10-1,000 Å thick, and most preferably from about 25 to 200 Å thick.

[0025] In certain example embodiments of this invention, temporary protective layer(s) 29 is of or includes diamond-like carbon (DLC). The DLC inclusive layer(s) 29 may be deposited on substrate 1 over coating 27 using an ion beam source, or any other suitable technique. For example, any of the DLC layer(s) (and corresponding deposition techniques) disclosed in any of U.S. Patent Nos. 6,335,086, 6,261,693, 6,303,225, 6,303,226, 5,635,245, 5,527,596, or 5,508,092 (all hereby incorporated herein by reference) may be used to form layer(s) 29. Alternatively, any other suitable type of DLC may be used in layer(s) 29 in other embodiments of this invention. Temporary protective layer(s) 29 may include one or more layers in different embodiments of this invention. While protective layer 29 preferably comprises DLC in certain embodiments of this invention, this invention is not so limited; in particular, layer 29 may be of or include any other suitable material that is capable of protecting coating 27 from scratching and can at least partially burn off during heat treatment.

[0026] After substrate 1 has been coated with both solar control coating 27 and DLC layer(s) 29 (see Fig. 3(b)), the coated article may be processed (e.g.,

shipped, moved, cut, cleaned, seamed, washed, and/or the like) (see step C in Fig. 4). As shown in Fig. 3(c), the coated article is then subjected to heat treatment (e.g., thermal tempering, heat bending, and/or heat strengthening); and during this heat treatment the DLC layer(s) 29 burns off either in part or entirely (see step D in Fig. 4) (it is noted that the DLC may tend to burn off at a temperature of about 400 degrees C). Such heat treatment may, in certain example embodiments of this invention, involve heating the coated substrate to temperature(s) of at least about 570 degrees C; more preferably from 1100°F (593°C) up to 1450°F (788°C) (more preferably from about 1100 to 1200 degrees F, and most preferably from 1150-1200 degrees F) for a sufficient period of time (e.g., at least 1 minute, more preferably at least 5 minutes) to achieve the end result (e.g., tempering, bending, layer 29 burn-off, and/or heat strengthening). Fig. 3(c) illustrates that after this heat treatment, much or all of the DLC inclusive layer 29 is no longer present on the coated article since it has burned off during the heat treatment.

[0027] After heat treatment (and thus after the DLC layer 29 has at least partially burned off), the coated substrate (i.e., substrate 1 with the solar control coating 27 thereon) is coupled to another substrate 2 in order to form the resulting window unit (see step E in Fig. 4). Example resulting window units are shown in Figs. 1, 2 and 3(d).

[0028] As will be explained below, DLC is hard and serves to protect the coating 27 from scratches and the like during the processing period between the coating and heat treating stages of the manufacturing process. However, addition of the DLC layer(s) 29 to the coated article tends to reduce the visible transmission of the article. Thus, according to certain embodiments of this invention, the DLC layer(s) 29 is useful for protection purposes during the manufacturing process (its reduction in visible transmission is irrelevant during production), and it can be removed (e.g., burned off) during heat treatment. It will be appreciated that the visible transmission of the coated article increases when the DLC layer(s) 29 is burned off, prior to formation of the final window unit.

[0029] In certain example embodiments of this invention, when DLC for example is provided in temporary protective layer(s) 29, the layer(s) 29 includes has



an average hardness of at least about 10 GPa, more preferably at least about 20 GPa, and most preferably from about 20-90 GPa. Such hardness renders layer (s) 29 resistant to scratching, certain solvents, and/or the like. Layer 29 may, in certain example embodiments where DLC is used, include more  $sp^3$  carbon-carbon (C - - C) bonds than  $sp^2$  carbon-carbon (C - - C) bonds. In certain example embodiments at least about 50% of the carbon-carbon bonds in the layer 29 may be  $sp^3$  carbon-carbon (C - - C) bonds, more preferably at least about 60% of the carbon-carbon bonds in the layer 29 may be  $sp^3$  carbon-carbon (C - - C) bonds, and most preferably at least about 70% of the carbon-carbon bonds in the layer 29 may be  $sp^3$  carbon-carbon (C - - C) bonds. In such embodiments, the DLC may be a special type of DLC known as highly tetrahedral amorphous carbon (ta-C) (which may or may not be hydrogenated or otherwise doped) (e.g., see U.S. Patent No. 6,261,693, which is incorporated herein by reference). In certain example embodiments of this invention, the DLC may have a density of at least about  $2.4 \text{ gm/cm}^3$ , more preferably of at least about  $2.7 \text{ gm/cm}^3$ . Example linear ion beam sources that may be used to deposit DLC inclusive layer 29 on substrate 1 include any of those in any of U.S. Patent Nos. 6,261,693, 6,002,208, 6,335,086, or 6,303,225 (all incorporated herein by reference). When using an ion beam source to deposit layer(s) 29, hydrocarbon feedstock gas(es) (e.g.,  $C_2H_2$ ), HMDSO, or any other suitable gas, may be used in the ion beam source in order to cause the source to emit an ion beam toward substrate 1 for forming layer(s) 29 over coating 27. It is noted that the hardness and/or density of layer(s) 29 may be adjusted by varying the ion energy of the depositing apparatus.

[0030] As discussed above, any suitable type of solar control coating 27 may be used in different embodiments of this invention. For purposes of example, and without limitation, two example solar control coatings 27 are illustrated in Figs. 5-6. Each of Figs. 5 and 6 shows an example solar control coating 27 provided on a substrate between the substrate 1 and the DLC inclusive temporary protective layer 29 (i.e., at the Fig. 3(b) stage of the manufacturing process).

[0031] The example solar control coating 27 according to the Fig. 5 embodiment includes first dielectric layer 3, second dielectric layer 5, first lower contact layer 7 (which contacts layer 9), first conductive metallic infrared (IR)

reflecting layer 9, first upper contact layer 11 (which contacts layer 9), third dielectric layer 13 (which may be deposited in one or multiple steps in different embodiments of this invention), fourth dielectric layer 15, second lower contact layer 17 (which contacts layer 19), second conductive metallic IR reflecting layer 19, second upper contact layer 21 (which contacts layer 19), fifth dielectric layer 23, and finally sixth protective dielectric layer 25. The "contact" layers each contact at least one IR reflecting layer. The aforesaid layers make up heat treatable low-E (i.e., low emissivity) coating 27 which is provided on substrate 1. The coating 27 is preferably deposited on substrate 1 via sputtering, although other deposition techniques may also be used.

[0032] In certain examples embodiments, the coating 27 according to the Fig. 5 embodiment may be as in the Table 1 below.

Table 1 (Example Materials/Thicknesses; Fig. 5 Embodiment)

Layer	Preferred Range (Å)	More Preferred (Å)	Example (Å)
TiO <sub>2</sub> (layer 3)	0-400 Å	50-250 Å	100 Å
Si <sub>x</sub> N <sub>y</sub> (layer 5)	0-400 Å	50-250 Å	170 Å
NiCrO <sub>x</sub> (layer 7)	5-100 Å	10-50 Å	18 Å
Ag (layer 9)	50-250 Å	80-120 Å	105 Å
NiCrO <sub>x</sub> (layer 11)	5-100 Å	10-50 Å	16 Å
SnO <sub>2</sub> (layer 13)	0-800 Å	500-850 Å	650 Å
Si <sub>x</sub> N <sub>y</sub> (layer 15)	0-800 Å	50-250 Å	170 Å
NiCrO <sub>x</sub> (layer 17)	5-100 Å	10-50 Å	18 Å
Ag (layer 19)	50-250 Å	80-120 Å	105 Å
NiCrO <sub>x</sub> (layer 21)	5-100 Å	10-50 Å	16 Å
SnO <sub>2</sub> (layer 23)	0-500 Å	100-300 Å	150 Å
Si <sub>3</sub> N <sub>4</sub> (layer 25)	0-500 Å	100-300 Å	250 Å

[0033] Figure 6 illustrates a low-E heat treatable coating 27 according to another embodiment of this invention. The Fig. 6 coating 27 is the same as the Fig. 5 coating described above, except that either (i) dielectric layer 3 is removed, or (ii) layers 3 and 5 are replaced with a single silicon nitride layer 40. Silicon nitride layer 40 may be of or include  $\text{Si}_3\text{N}_4$  in certain embodiments of this invention. In other embodiments, silicon nitride layer 40 may be of or include  $\text{Si}_x\text{N}_y$  where  $x/y$  may be from about 0.65 to 0.80, or alternatively from about 0.76 to 1.5 in silicon rich embodiments. Additional details regarding the coatings 27 of Figs. 5-6, including example sputter process parameters for forming the coatings, may be found in U.S. Patent Application Serial No. 09/794,224 (hereby incorporated herein by reference).

[0034] In certain exemplary embodiments of this invention, solar control coatings 27 may have one or more of the following characteristics before/after heat treatment (HT) when in monolithic form, as set forth in Table 2:

Table 2: Coating 27 Monolithic Before/After Heat Treatment (HT)

Characteristic	General	More Preferred	Most Preferred
$R_s$ (ohms/sq.)(before HT):	$\leq 40.0$	$\leq 20.0$	$\leq 8.0$
$R_s$ (ohms/sq.)(after HT):	$\leq 40.0$	$\leq 20.0$	$\leq 8.0$
$E_n$ (before HT):	$\leq 0.30$	$\leq 0.20$	$\leq 0.08$
$E_n$ (after HT):	$\leq 0.30$	$\leq 0.20$	$\leq 0.08$

[0035] The example coatings 27 are provided for purposes of example and without limitations. Other suitable solar control coatings may instead be used in other embodiments of this invention. With regard to Figs. 5-6, it is noted that each of these coatings 27 includes a pair of metallic silver (Ag) layers 9, 19 which function to reflect IR and UV radiation, in order to achieve low-E characteristics.

[0036] In certain embodiments of this invention, it is noted that other layers (e.g., a tie layer or the like) may be provided between the DLC inclusive layer 29 and

coating 27. Such a layer(s) may or may not burn off along with layer 29 during heat treatment.

[0037] While the temporary layer 29 comprises DLC in many embodiments discussed above, certain embodiments of this invention are not so limited. For example, protective paint may be used instead of DLC for layer 29 in certain embodiments of this invention, can be burned off in a similar manner.

[0038] While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiments, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

## CLAIMS

1. A method of making a window unit, the method comprising:  
providing a coating on a glass substrate, the coating including at least one layer comprising Ag;  
depositing a protective layer comprising diamond-like carbon (DLC) on the glass substrate over the coating;  
heat treating the glass substrate with the coating and protective layer thereon so that the protective layer comprising diamond-like carbon (DLC) at least partially burns off during the heat treating; and  
following said heat treating, coupling the glass substrate with the coating thereon to another substrate in order to form the window unit.
2. The method of claim 1, wherein the window unit is an insulating glass (IG) window unit.
3. The method of claim 1, wherein said coupling comprises laminating the glass substrate to the another substrate via a polymer inclusive interlayer in order to form a vehicle windshield.
4. The method of claim 1, wherein said heat treating comprises heating the glass substrate to a temperature of at least about 570<sup>0</sup> C.
5. The method of claim 4, wherein said heat treating comprises heating the glass substrate to a temperature of from about 590<sup>0</sup> C to 788<sup>0</sup> C for at least one minute in thermally tempering and/or heat bending the glass substrate.
6. The method of claim 1, wherein the protective layer comprising DLC entirely burns off during the heat treatment.
7. The method of claim 1, wherein the protective layer comprising DLC is deposited on the glass substrate over the coating via ion beam deposition using a hydrocarbon inclusive gas in an ion beam source.

8. The method of claim 1, wherein the protective layer comprising DLC has an average hardness of at least about 10 GPa.
9. The method of claim 8, wherein the protective layer comprising DLC has an average hardness of at least about 20 GPa.
10. The method of claim 1, wherein the protective layer comprising DLC includes more  $sp^3$  carbon-carbon bonds than  $sp^2$  carbon-carbon bonds.
11. The method of claim 1, wherein the coating comprises a second layer comprising Ag, and wherein the two layers comprising Ag in the coating are spaced from one another with at least one dielectric layer provided therebetween.
12. The method of claim 1, wherein the dielectric layer comprises at least one of tin oxide and silicon nitride.
13. A method of making a window unit, the method comprising:
  - providing a solar control coating on a glass substrate;
  - ion beam depositing a protective layer comprising diamond-like carbon (DLC) on the glass substrate over the coating;
  - heat treating the substrate with the coating and protective layer thereon at a temperature of at least 570 degrees C so that the protective layer comprising diamond-like carbon (DLC) at least partially burns off; and
  - following said heat treating, coupling the glass substrate with the coating thereon to another substrate in order to form the window unit.
14. The method of claim 13, wherein the window unit comprises at least one of an IG window unit and a vehicle windshield.
15. The method of claim 13, wherein the solar control coating comprises at least one layer comprising Ag, and at least first and second dielectric layers on opposites sides of the layer comprising Ag.
16. A method of making a window unit, the method comprising:
  - providing a solar control coating on a glass substrate;

depositing at least one temporary protective layer on the glass substrate over the coating;

heat treating the substrate with the coating and protective layer thereon at a temperature of at least 570 degrees C so that the protective layer burns off; and

following said heat treating, coupling the glass substrate with the coating thereon to another substrate in order to form the window unit.

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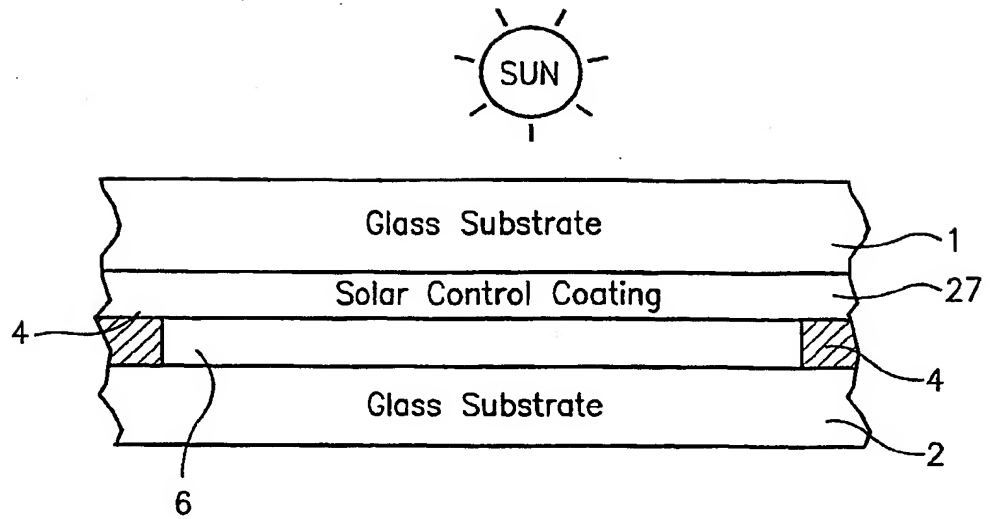


FIG. 1

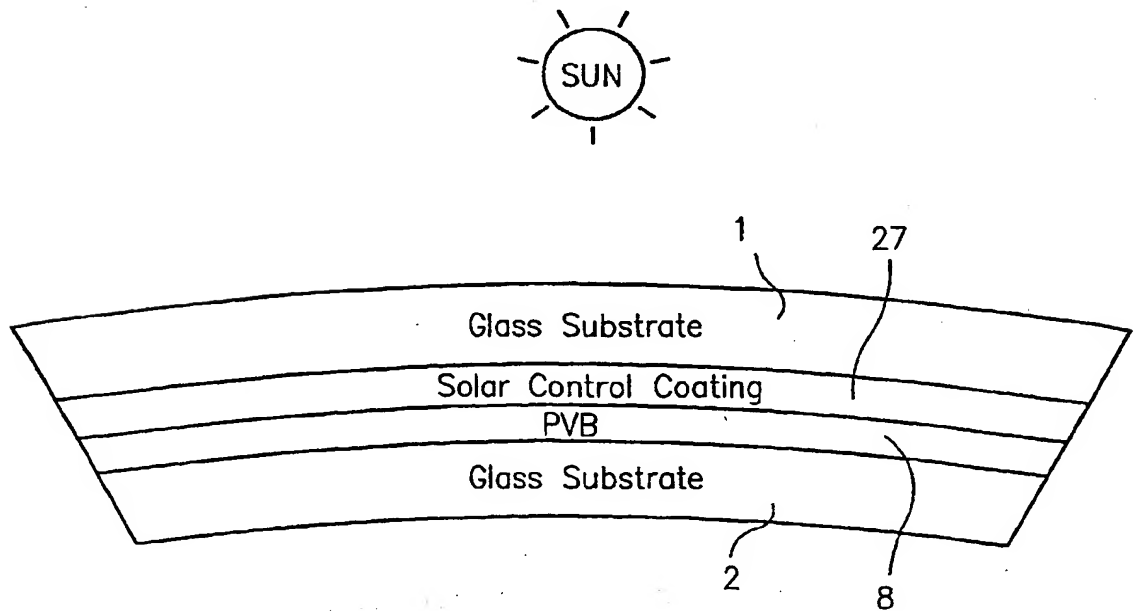


FIG. 2

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FIG. 3(a)

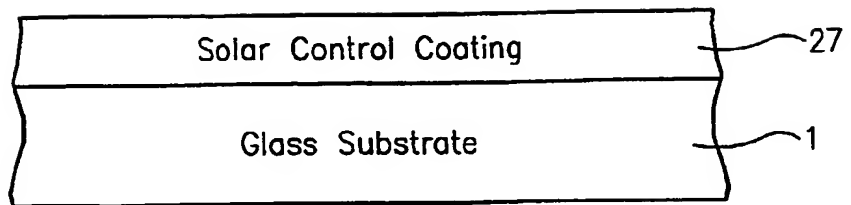


FIG. 3(b)

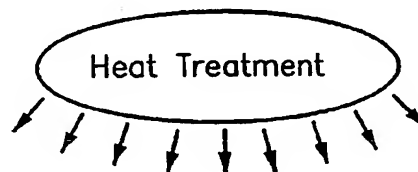
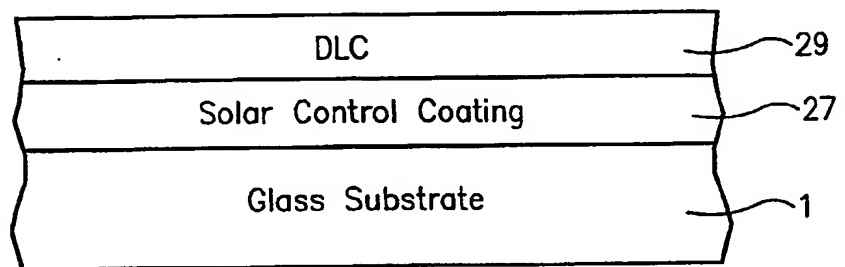


FIG. 3(c)

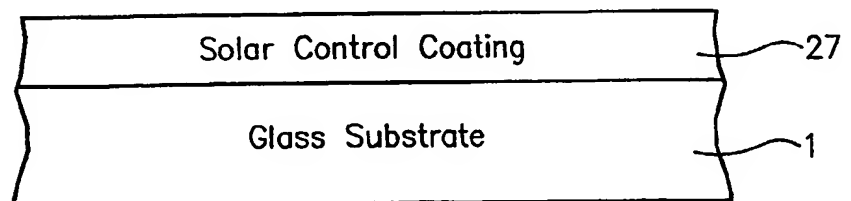
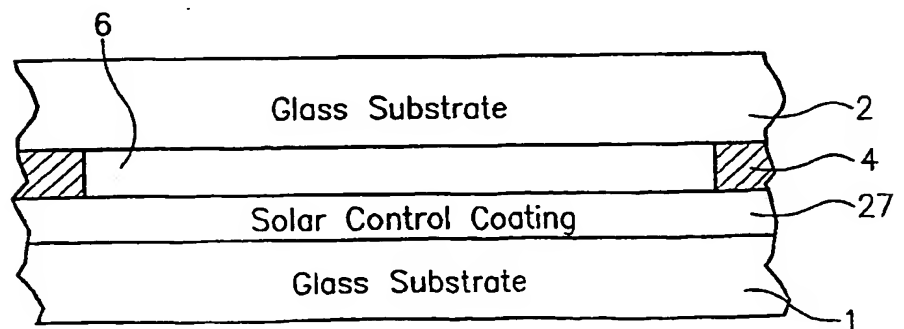


FIG. 3(d)



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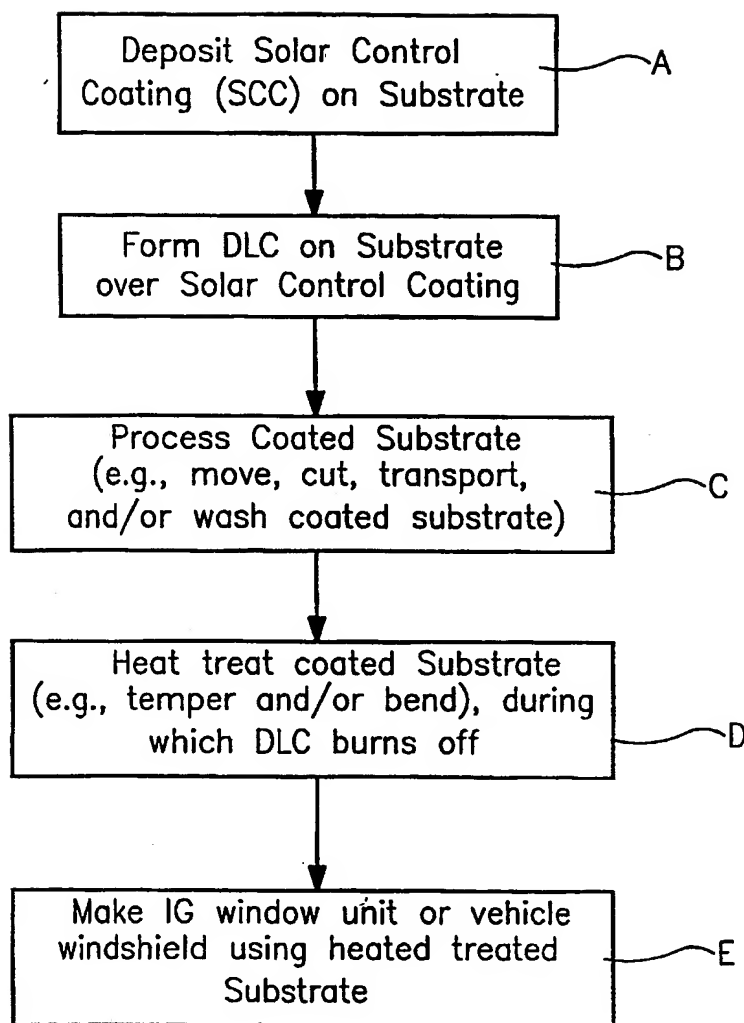


FIG. 4

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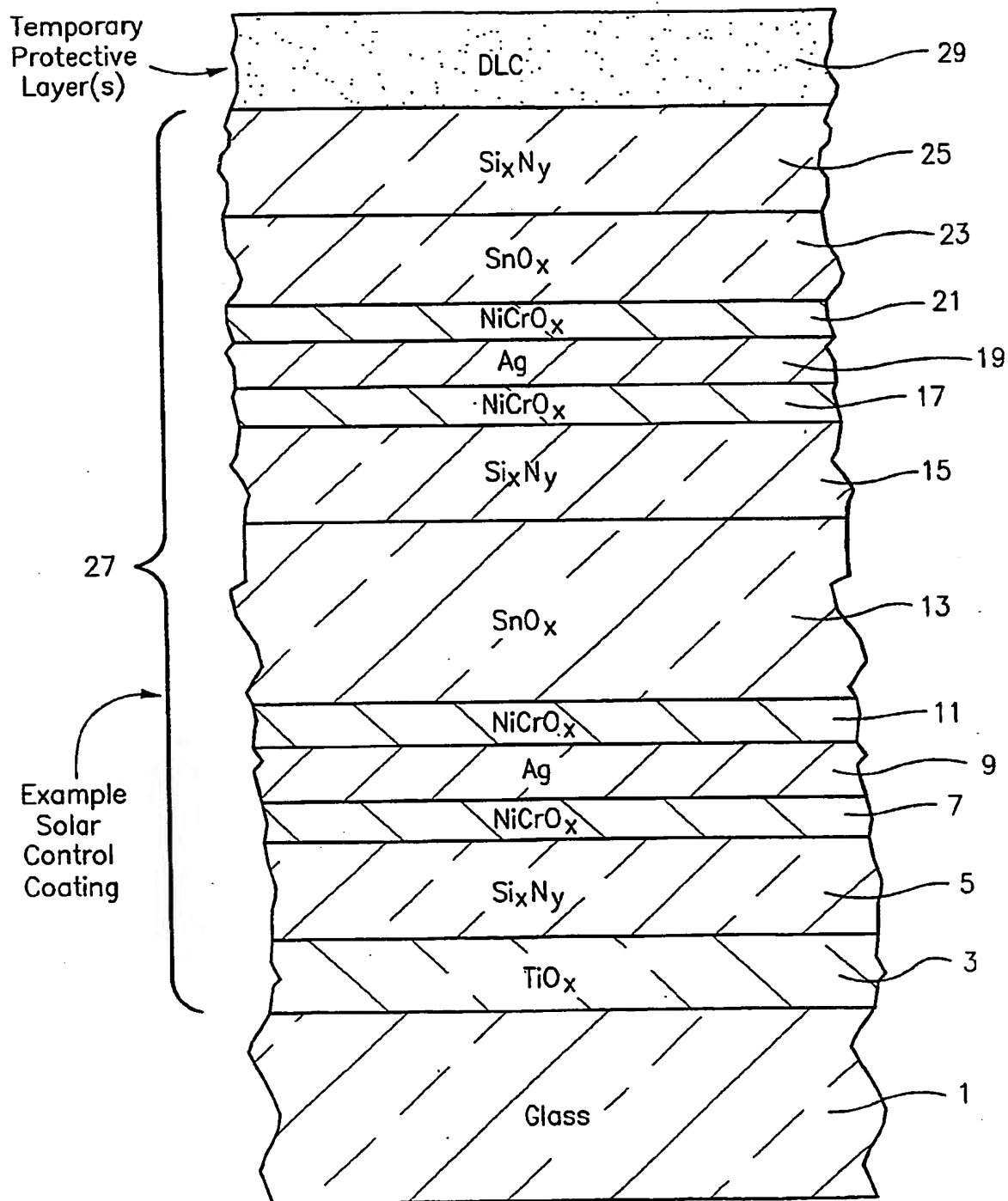


FIG. 5

SUBSTITUTE SHEET (RULE 26)

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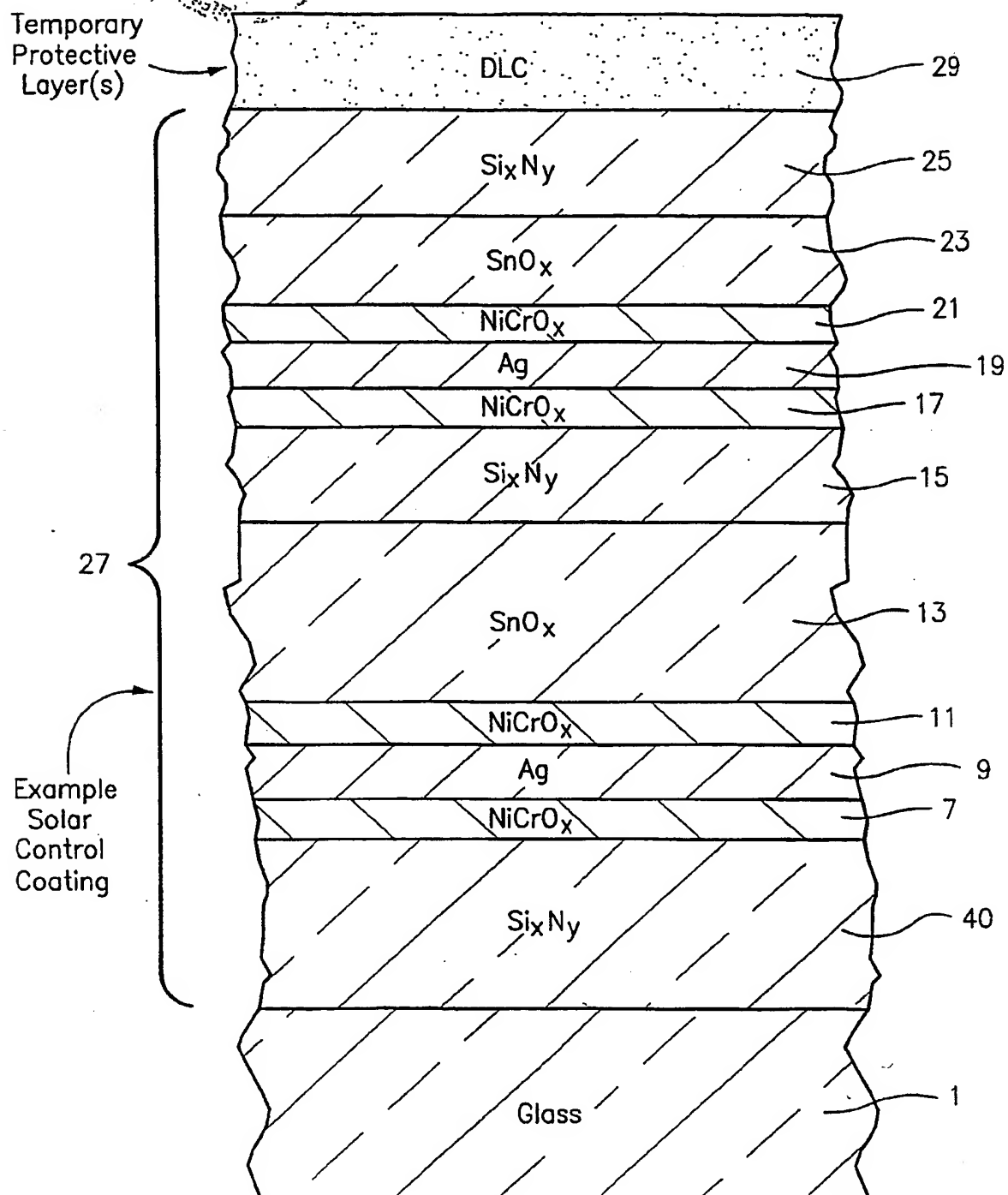


FIG. 6

SUBSTITUTE SHEET (RULE 26)

## INTERNATIONAL SEARCH REPORT

Intern: Application No

PCT, 03/04239

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B17/10 C03C23/00 C03C17/22 C23C16/26 C03C17/34  
 C03C17/36 E06B3/66

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B C03C C23C B05D G02B B08B E06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 261 693 B1 (VEERASAMY VIJAYEN S) 17 July 2001 (2001-07-17)  column 4, line 55 -column 5, line 13; figure 3 column 7, line 50 -column 9, line 10 column 7, line 26 - line 62	1,3,4, 7-10,13, - 16
Y	US 2002/001718 A1 (VEERASAMY VIJAYEN S) 3 January 2002 (2002-01-03)  page 3, paragraphs 46,48,50,52 page 4, paragraph 60 -page 5, paragraph 64 claims 15-18,43,44  -/--	1,3,4, 7-10, 13-16

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

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PCT. 03/04239

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 605 814 A (IBM) 13 July 1994 (1994-07-13)  page 6, column 8, line 57 -page 7, column 9, line 26 page 7, column 10, line 22-46 ----	1,3,4, 7-10, 13-16
E	WO 03 033427 A (GUARDIAN INDUSTRIES) 24 April 2003 (2003-04-24) page 5, paragraph 60; figure 3 page 7, paragraph 70; figure 11 page 8, paragraph 73; figure 13B page 6, paragraph 64 ----	1,3-7, 13,16
X		11,12,15
A	US 6 180 247 B1 (RUSKE MANFRED ET AL) 30 January 2001 (2001-01-30) column 1, line 6 -column 2, line 62 tables I,II ----	1,8,9, 13,15,16
A	WEILER M ET AL: "PREPARATION AND PROPERTIES OF HIGHLY TETRAHEDRAL HYDROGENATED AMORPHOUS CARBON" PHYSICAL REVIEW, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 53, no. 3, 15 January 1996 (1996-01-15), pages 1594-1608, XP000992913 page 1598, paragraph V -page 1603 ----	1,8,9, 13,16
A	US 4 882 827 A (UNO KEN ET AL) 28 November 1989 (1989-11-28) column 1, line 13 -column 2, line 25 column 4, line 41 -column 6, line 28 -----	1,4,5,7, 13,16

## INTERNATIONAL SEARCH REPORT

Inte. cation No  
PC... 04239

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6261693	B1	17-07-2001	
		AT 236860 T	15-04-2003
		AU 4811300 A	17-11-2000
		BR 0008391 A	29-01-2002
		CA 2368471 A1	09-11-2000
		CZ 20013760 A3	15-05-2002
		DE 60002060 D1	15-05-2003
		EP 1177156 A1	06-02-2002
		HU 0200949 A2	29-07-2002
		JP 2002543035 T	17-12-2002
		US 2002081378 A1	27-06-2002
		WO 0066506 A1	09-11-2000
		US 2002155294 A1	24-10-2002
		US 2002192371 A1	19-12-2002
		US 2003064198 A1	03-04-2003
		US 2003021997 A1	30-01-2003
		US 6338901 B1	15-01-2002
		US 6273488 B1	14-08-2001
		US 6284377 B1	04-09-2001
		US 6335086 B1	01-01-2002
		US 6312808 B1	06-11-2001
		US 6280834 B1	28-08-2001
		US 6277480 B1	21-08-2001
		US 6447891 B1	10-09-2002
		US 6461731 B1	08-10-2002
		US 6475573 B1	05-11-2002
		US 6368664 B1	09-04-2002
		US 2001014398 A1	16-08-2001
		US 2001035662 A1	01-11-2001
		US 2001028956 A1	11-10-2001
		US 2001053412 A1	20-12-2001
		US 2001044030 A1	22-11-2001
		US 2001051273 A1	13-12-2001
		US 2002001718 A1	03-01-2002
		US 2002012798 A1	31-01-2002
		US 2002009593 A1	24-01-2002
		US 2002028289 A1	07-03-2002
US 2002001718	A1	03-01-2002	
		US 6303225 B1	16-10-2001
		US 6284377 B1	04-09-2001
		US 6338901 B1	15-01-2002
		US 6261693 B1	17-07-2001
		US 2002127404 A1	12-09-2002
		AU 6178001 A	03-12-2001
		EP 1289898 A1	12-03-2003
		WO 0190016 A1	29-11-2001
		AU 5558701 A	07-11-2001
		WO 0181261 A1	01-11-2001
		US 2001051273 A1	13-12-2001
		AU 1604301 A	30-05-2001
		BR 0015667 A	23-07-2002
		CA 2390256 A1	25-05-2001
		EP 1248747 A2	16-10-2002
		JP 2003514746 T	22-04-2003
		US 2002081378 A1	27-06-2002
		WO 0136342 A2	25-05-2001
		US 2002155294 A1	24-10-2002
		US 2002192371 A1	19-12-2002
		US 2003064198 A1	03-04-2003

## INTERNATIONAL SEARCH REPORT

Inte	ication No
PC	'04239

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002001718 A1		US 2003021997 A1	30-01-2003
		US 6273488 B1	14-08-2001
		US 6335086 B1	01-01-2002
		US 6312808 B1	06-11-2001
		US 6280834 B1	28-08-2001
		US 6277480 B1	21-08-2001
		US 6447891 B1	10-09-2002
		US 6461731 B1	08-10-2002
		US 6475573 B1	05-11-2002
		US 6368664 B1	09-04-2002
		US 2001035662 A1	01-11-2001
		US 2001028956 A1	11-10-2001
		US 2001053412 A1	20-12-2001
		US 2001044030 A1	22-11-2001
		US 2002009593 A1	24-01-2002
		US 2002028289 A1	07-03-2002
		AT 236860 T	15-04-2003
		AU 4811300 A	17-11-2000
		BR 0008391 A	29-01-2002
		CA 2368471 A1	09-11-2000
		CZ 20013760 A3	15-05-2002
		DE 60002060 D1	15-05-2003
		EP 1177156 A1	06-02-2002
		HU 0200949 A2	29-07-2002
		JP 2002543035 T	17-12-2002
		WO 0066506 A1	09-11-2000
		US 2001014398 A1	16-08-2001
		US 2002012798 A1	31-01-2002
EP 0605814 A	13-07-1994	US 5470661 A	28-11-1995
		DE 69304503 D1	10-10-1996
		EP 0605814 A1	13-07-1994
		JP 2553310 B2	13-11-1996
		JP 7242493 A	19-09-1995
		US 5569501 A	29-10-1996
WO 03033427 A	24-04-2003	WO 03033427 A1	24-04-2003
US 6180247 B1	30-01-2001	DE 19850023 A1	04-05-2000
		AT 233720 T	15-03-2003
		DE 59904431 D1	10-04-2003
		EP 0999192 A1	10-05-2000
		JP 2000143297 A	23-05-2000
US 4882827 A	28-11-1989	JP 1083529 A	29-03-1989
		JP 1831226 C	15-03-1994
		JP 4061816 B	02-10-1992
		DE 3832907 A1	20-04-1989